

Docket No.: H0610.0353/P353  
(PATENT)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of:  
Niels Erikstrup, et al.

Application No.: Not Yet Assigned

Filed: Concurrently Herewith

Art Unit: N/A

For: PROCESS FOR THE PREPARATION OF  
SYNTHESIS GAS

Examiner: Not Yet Assigned

**CLAIM FOR PRIORITY AND SUBMISSION OF DOCUMENTS**

MS Patent Application  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

Applicant hereby claims priority under 35 U.S.C. 119 based on the following prior foreign applications filed in the following foreign countries on the dates indicated:

<u>Country</u>	<u>Application No.</u>	<u>Date</u>
Denmark	PA 2002 01433	September 26, 2002
Denmark	PA 2002 01434	September 26, 2002

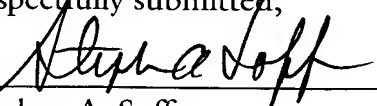
Application No.: Not Yet Assigned

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In support of this claim, a certified copy of each said original foreign application is filed herewith.

Dated: September 25, 2003

Respectfully submitted,

By 

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Patent application No.: PA 2002 01433

Date of filing: 26 September 2002

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Denmark

Title: Fremgangsmåde til fremstilling af syntesegas

IPC: C01B 3/38; B01J 8/02

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



**Patent- og Varemærkestyrelsen**  
Økonomi- og Erhvervsministeriet

15 August 2003

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Process for the Preparation of Synthesis Gas

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The invention concerns a process for the preparation of synthesis gas from a hydrocarbon containing feedstock in an autothermal reformer (ATR) and heat exchange reformer operated in parallel with addition of carbon monoxide rich gas to the feedstock.

### Description of the Invention

A plant for production of synthetic diesel and other synthetic hydrocarbons consists of three main parts. In the first main unit synthesis gas (a mixture of hydrogen and carbon oxides) is produced from the feedstock which is usually natural gas or a similar light hydrocarbon feedstock. In the second main unit, the actual hydrocarbon synthesis takes place usually by the Fischer-Tropsch synthesis. In the final part often known as product workup unit (PWU) the raw products are refined and/or separated to give the desired end products. The present invention relates to an improved method for production of synthesis gas.

Today, one of the most cost effective and efficient methods for production of synthesis gas is by Autothermal Reforming (ATR). In ATR the light hydrocarbon feedstock with addition of steam reacts with a sub-stoichiometric amount of oxygen to produce synthesis gas. An ATR reactor consists of a burner, a combustion chamber, and a catalyst bed in a refractory lined pressure shell.

For the Fischer-Tropsch synthesis to be as effective as possible, a specific synthesis gas composition is often desired. In many cases the desired synthesis gas composition is given by the ratio of the content of hydrogen to the

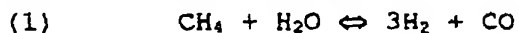
content of carbon monoxide. The desired ratio is often approximately 2.0. With most operating conditions ATR is not able to produce this ratio. Instead a carbon dioxide containing stream must be recirculated to a location upstream the ATR reactor. This recirculation stream is often a tail gas, which is essentially a by-product from the Fischer-Tropsch synthesis unit and/or the Product Work-up unit.

The main components in the tail gas are carbon monoxide, carbon dioxide, hydrogen and various light hydrocarbons such as methane, ethane, propane, ethylene and propylene.

Synthesis gas production may account for more than 50% of the total capital cost in a Fischer-Tropsch plant. For a plant based on ATR a large fraction of the cost of the synthesis gas production unit arises from the air separation unit needed to produce oxygen. Hence, there is a considerable interest in methods for reducing the oxygen consumption per unit of synthesis gas produced.

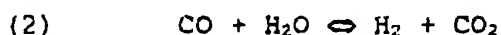
The installation of a heat exchange steam reforming unit (HESRU) in parallel with the ATR is one method for increasing the synthesis gas production without the corresponding need for a larger air separation unit. In this case the feed (typically a mixture of desulphurised natural gas and steam or a pre-reformed mixture) is split between the ATR and the HESRU. The tail gas is added either to the ATR feed stream, the HESRU feed stream or to both feed streams. The effluents from the ATR and the HESRU are combined to give the synthesis gas, which is sent to the Fischer-Tropsch synthesis section.

In the HESRU the endothermic steam reforming reaction of the hydrocarbons take place as illustrated below, using methane as an example:



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The steam reforming reactions are accompanied by the water gas shift reaction:



10 The above two reactions are close to equilibrium at the HESRU outlet. The temperature of the exit gas is above 800°C to ensure a satisfactory methane conversion. The amount of tail gas added is adjusted to give the desired exit gas composition. Typically, the installation of the  
15 HESRU will increase the amount of tail gas recirculated to the process.

As described above, the HESRU reduces the oxygen consumption. However, the HESRU itself may be quite cost intensive  
20 and methods for reducing the size are desired. The catalyst in steam reforming units is often nickel supported on ceramic carriers such as alumina.

Steam reforming involves the risk of detrimental carbon  
25 formation on the catalyst such as (example for methane):



Detrimental carbon formation on the catalyst may result in catalyst breakage, catalyst deactivation, and will eventually  
30 block the flow passage and must be avoided. One method known in the art to avoid carbon formation is to add a sufficient amount of steam to the hydrocarbon process stream.

However, in Fischer-Tropsch plants it is in general desirable to minimise the amount of steam added to the feedstock. One method for reducing the required amount of steam without carbon formation is to use noble metal catalysts (Rostrup-Nielsen et al., J.Catalysis 144, page 38, 1993). However, the cost of noble metals as compared to nickel is very high and considering the size of the HESRU it is desirable to reduce the amount of catalyst.

10 The general object of the invention is to provide a steam reforming process by which size of the HESRU and amount of steam reforming catalyst is reduced.

15 Accordingly, this invention is a process for the production of synthesis gas by catalytic steam reforming of a hydrocarbon containing feedstock in parallel in an autothermal steam reformer and in a heat exchange steam reformer in indirect heat exchange with a steam reformed effluent stream from the autothermal steam reformer and a steam reformed effluent from the heat exchange reformer, wherein a carbon monoxide containing gas is added to the hydrocarbon feedstock prior to steam reforming in the autothermal steam reformer and/or to the heat exchange steam reformer, the carbon monoxide containing gas is added in an amount resulting in a product stream in which the ratio of the amount of hydrogen to the amount of carbon monoxide is between 1.8 to 2.3.

25 The above features and aspects are disclosed in greater detail in the following description with reference to the drawings in which Fig. 1 shows a specific embodiment of the invention.



A hydrocarbon and steam containing feed stream (1) is split into a stream (5) and a stream (14) in a ratio determined on a case to case basis. Optionally, stream (14) can be pre-reformed and/or further heated (not shown in Fig. 1).

5 In case pre-reforming is carried out, this will be done by the use of an adiabatic pre-reformer as described in the art (Christensen, Appl. Cat.A, 138, page 285,1996)

10 Tail gas in a total amount to give the desired exit gas composition is added either through line (3) to line (14) or through line (2) to line (5) or through both lines in a ratio to be determined on a case to case basis. The combined stream (8) is together with oxidant (4) introduced into the ATR (13) to produce synthesis gas (9). The combined stream (6) is introduced into the HESRU (7) to produce synthesis gas (11). The synthesis gas streams (9) and (11) are combined to stream (12). Combination of the streams may be carried out inside a collector. Stream (12) provides the heat for the endothermic steam reforming reaction occurring in the HESRU.

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The catalyst in the HESRU (7) is in the form of catalysed hardware. The catalysed hardware can be applied directly to the surfaces through which heat transfer occurs in the HESRU. Catalysed hardware may further be in form of catalysts deposited in a metallic or ceramic structure attached to wall of the reactor. Alternatively, structured metallic or ceramic elements with a thin catalyst layer can be placed in the channels into which the feed stream (6) is introduced. The structured elements are preferably not straight channel monoliths as the heat transfer can be too

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low. Preferably the elements are cross-corrugated or of a similar nature.

The catalytic coating of a metal surface (wash coating) is a well known process (a description is given in e.g. Cybulski, A., and Moulijn, J. A., Structured catalysts and reactors, Marcel Dekker, Inc, New York, 1998, Chapter 3, and references herein). The appropriate material, preferably a ferritic steel containing Cr and/or Al, is heated to a temperature preferably above 800 C in order to form a layer of Cr and/or Al oxide. This layer facilitates a good adhesion of the ceramic to the steel. A thin layer of a slurry containing the ceramic precursor is applied on the surface by means of e.g. spraying, painting or dipping. After applying the coat the slurry is dried and calcined at a temperature usually in the region 350 - 1000 C. Finally the ceramic layer is impregnated with the catalytic active material. Alternatively the catalytic active material is applied simultaneously with the ceramic precursor. With catalysed hardware, the pressure drop is lower than with traditional catalyst pellets. Depending upon the actual plant or unit in question, this can be utilised to reduce the required pressure of the feed stream (1) while maintaining the same pressure in the product gas (10). Alternatively, the pressure drop from the inlet (6) to the outlet (11) can be maintained at the same level as in the case when pellets are used. In this case the pressure drop on the heat providing side (pressure in (12) minus the pressure in (10)) is increased. In this case the heat transfer area is substantially reduced since the heat transfer coefficient increases with increasing pressure drop. This will reduce the size and cost of the HESRU.

Also, in both cases, the amount of catalyst is substantially reduced as compared to the conventional schemes. The use of catalysed hardware implies that the amount of catalyst can be determined from the required catalytic activity. In conventional units using pellets, the reformer is designed to ensure sufficient heat transfer and pellets are simply placed in the tubes or channels through which the process gas flows often giving as known in the art a vast excess of catalyst activity.

In further an aspect of the invention, nickel catalyst is employed in areas, where the temperature is low, and noble metals are used in areas with higher temperatures, where risk of carbon formation on surface of the catalyst is higher.

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**CLAIMS**

1. Process for the production of synthesis gas by catalytic steam reforming of a hydrocarbon containing feedstock in parallel in an autothermal steam reformer and in a heat exchange steam reformer in indirect heat exchange with a steam reformed effluent stream from the autothermal steam reformer and a steam reformed effluent from the heat exchange reformer, wherein a carbon monoxide containing gas is added to the hydrocarbon feedstock prior to steam reforming in the autothermal steam reformer and/or to the heat exchange steam reformer, the carbon monoxide containing gas is added in an amount resulting in a product stream in which the ratio of the amount of hydrogen to the amount of carbon monoxide is between 1.8 to 2.3.
2. Process of claim 1, wherein the catalytic steam reforming in the heat exchange reformer is performed in presence of catalysed hardware.
3. Process of claim 2, wherein the catalysed hardware is placed on the surface of the walls of the heat exchange steam reformer in heat conducting relationship with the steam reformed effluent stream from the autothermal reformer and/or the steam reformed effluent stream from the heat exchange reformer.
4. Process of claim 2, wherein the catalysed hardware is placed on ceramic or metallic structured elements.
5. Process of claim 4, wherein the structured elements are cross-corrugated elements.

6. Process of claim 1, wherein active catalytic material is nickel, ruthenium, rhodium, iridium, platinum, palladium or any mixture thereof.

5 7. Process of claim 1, wherein the autothermal steam reforming is carried out with an oxidant containing at least 90% oxygen by volume.

8. Process of claim 1, wherein the hydrocarbon containing feedstock is a mixture of natural gas, steam, and hydrogen.

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9. Process of claim 1, wherein the hydrocarbon containing feedstock is a pre-reformed natural gas.

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10. Process of claim 1, wherein the carbon monoxide containing gas is tail gas from a Fischer-Tropsch process.

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**ABSTRACT**

5 Process for the production of synthesis gas by catalytic  
steam reforming of a hydrocarbon containing feedstock in  
parallel in an autothermal steam reformer and in a heat ex-  
change steam reformer in indirect heat exchange with a  
steam reformed effluent stream from the autothermal steam  
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change reformer, wherein a carbon monoxide containing gas  
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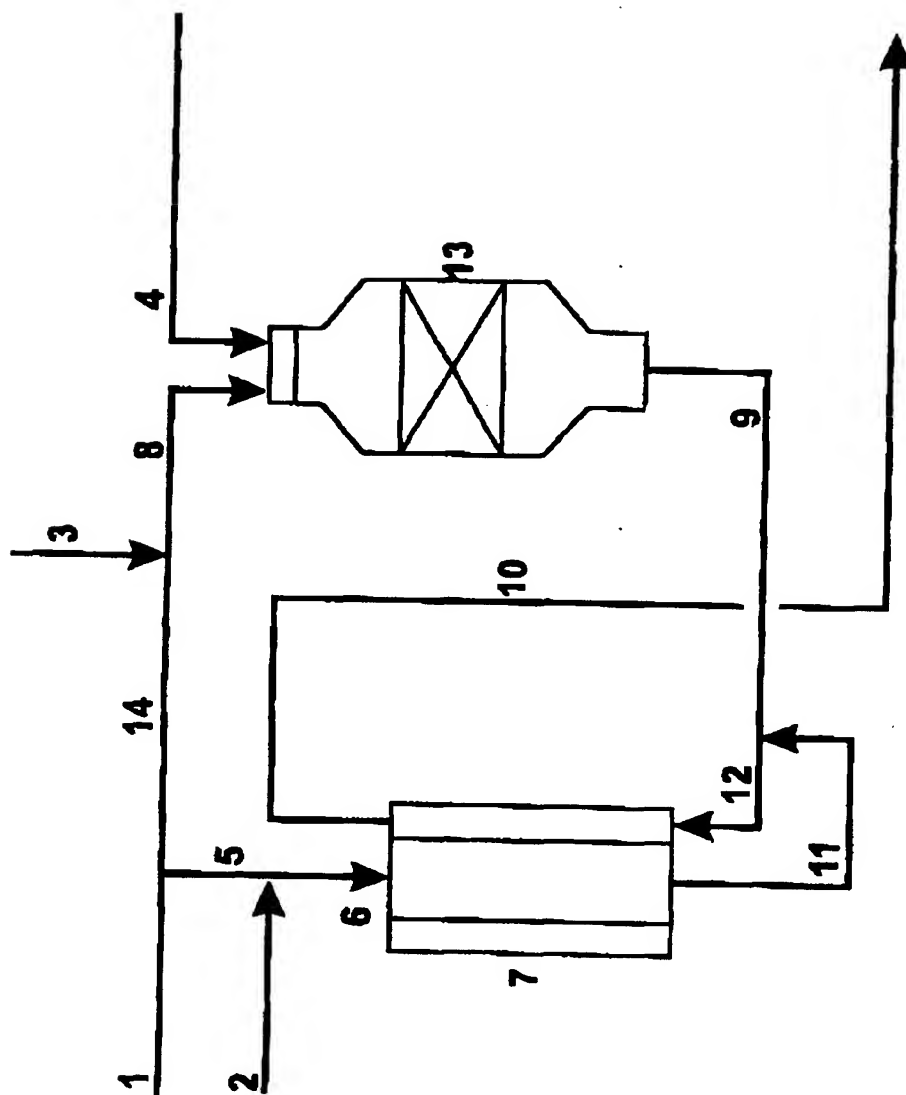


Fig. 1

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